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## Tilts and Ionic Shifts in Rhombohedral Perovskites

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We make a comparative analysis of rhombohedral perovskites ( $\text{ABO}_3$ ) with/without oxygen rotations and ionic shifts, within the framework of a generalised effective field approach. We analyse available data on  $\text{LaAlO}_3$  and  $\text{LiTaO}_3$  and new data on Zr-rich PZT, examples of three different ways of structural evolution with temperature of the rhombohedral perovskites. The coupling between polarization and tilt is studied in detail in PZT and a possible coupling between tilt and polarization in  $\text{LiTaO}_3$  is discussed.

### I. INTRODUCTION

The perovskite-based structures favour ferroelectricity due to the large Lorentz contributions in the dipolar internal field and to the intrinsic trend of the cations to displace inside the oxygen octahedra. On the other hand they show structural phase transitions related to the tilt of oxygen octahedra which allow a big variety of phases. The symmetry of the octahedra framework mainly determines that of the crystal lattice, justifying the classification of the perovskites by their tilt systems. The cation shifts and the octahedra tilts are independent and due to different kind of interactions, but they can be coupled. A model to explain this coupling has been proposed recently by the authors.

In the rhombohedral perovskites the tilt of the oxygen octahedra is about their triad axis and it can be described as  $a^-a^-a^-$ , according to Glazer's notation [2], which means opposite rotation for adjacent octahedra along each direction. Two space groups,  $R3c$  and  $R\bar{3}c$ , can sustain this tilt system. The first space group has a polar symmetry allowing ferroelectricity, while the second one is non-polar keeping the cation in the inversion centre. Rhombohedral perovskites in the space group  $R3m$  can also be found which do not present octahedra tilts and inversion centre.

The sequence of space groups presented by rhombohedral perovskites with temperature before reaching the cubic ( $\text{Pm}\bar{3}\text{m}$ ) phase, can, in principle, show the different combinations of these space groups that are allowed by symmetry. Polar  $R3m$  and tilted  $R\bar{3}c$  structures can transform straight to the cubic phase by increasing temperature. Polar and tilted space group,  $R3c$ , contains the  $R\bar{3}c$  and  $R3m$  symmetries and it has two possible ways to achieve the cubic phase, either  $R3c \rightarrow R\bar{3}c \rightarrow \text{Pm}\bar{3}\text{m}$  or  $R3c \rightarrow R3m \rightarrow \text{Pm}\bar{3}\text{m}$ . Examples of these two cases are  $\text{LiTaO}_3$  and PZT, respectively, although  $\text{LiTaO}_3$ , as well as  $\text{LiNbO}_3$ , does not show the cubic perovskite

phase before melting. Examples, such as  $\text{LaAlO}_3$ , of rhombohedral perovskites showing only tilts in the low temperature phase, i.e. showing a  $R\bar{3}c \rightarrow \text{Pm}\bar{3}\text{m}$  transitions, have been observed. Nevertheless, as far as we know, it has not been found any rhombohedral perovskite having solely a  $R3m \rightarrow \text{Pm}\bar{3}\text{m}$  phase transition, which implies no oxygen rotations in the whole range of temperature. A candidate for checking this possibility would be PZT compositions close to the morphotropic phase boundary. A Zr/Ti = 60/40 composition of PZT presents the  $R3c \rightarrow R3m$  transition as low as 250 K, but rhombohedral compositions with higher Zr content are difficult to characterise due to the high diffusion and the mixture of phases (rhombohedral and tetragonal) in this region. It is known that the disappearance of the oxygen rotations in PZT through the  $F_{\text{RL}}(R3c) \rightarrow F_{\text{RH}}(R3m)$  phase transition at  $T_{\text{LH}}$ , produces a step in the polarization curve. It means that there is some coupling of the octahedra tilts with the cation shifts. In this work we compare the three mentioned examples: PZT (cation shifts+tilts  $\rightarrow$  cation shifts  $\rightarrow$  cubic),  $\text{LiTaO}_3$  (cation shifts+tilts  $\rightarrow$  tilts  $\rightarrow$  melting) and  $\text{LaAlO}_3$  (tilts  $\rightarrow$  cubic). We study the behaviour of the two independent order parameters, related to polarization ( $p_s$ ) and rotation angle ( $\eta_s$ ), and the coupling between them.

We have used available data of paramagnetic resonance in  $\text{LaAlO}_3$  by K. A. Müller et al. The spontaneous polarization of  $\text{LiTaO}_3$  is from pyroelectric current data by A. M. Glass, while the structural data of  $\text{LiTaO}_3$  are from S. C. Abrahams et al. Experimental data of PZT are described in the next section.

### II. EXPERIMENTAL

Ceramic PZT samples used were made at the Shanghai Institute of Ceramics. The composition belongs to

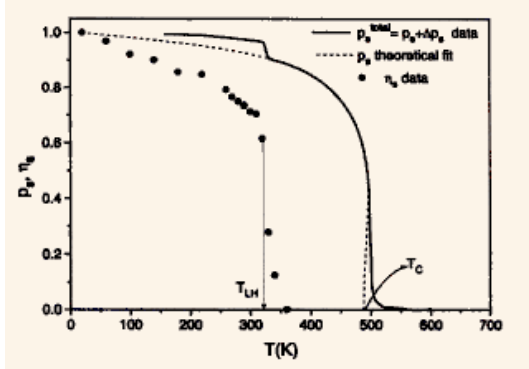


Fig. 1. Order parameters ( $p_s$  and  $\eta_s$ ) from pyroelectric discharge and neutron data, respectively, are plotted versus temperature for rhombohedral PZT. The  $p_s$  fit was made using the generalised effective field approach. We label  $p_s^{\text{total}} = p_s + \Delta p_s$  the sum of the polarization without tilt ( $p_s$ ) and the extra polarization ( $\Delta p_s$ ) appearing with the tilt.

the rhombohedral region with a very high Zr content (Zr/Ti= 96.5/3.5). 1.5 wt% of  $\text{Nb}_2\text{O}_5$  was added to improve the electrical properties. The constituent oxides were ground, pressed into pellets, and fired at 1350 °C for 2 h. Cylinders of about 1 cm in height and 1 cm in diameter were sintered and hot pressed for the neutron diffraction runs [3]. The same procedure has been used, more recently, for the preparation of thin plates of the same nominal composition, of 1 mm in thickness and about 1 cm in diameter, which were used for the pyroelectric measurements.

Neutron data used in this work were presented recently by the authors [3]. They were taken with neutron of 14.7 meV energy at Brookhaven National Laboratory. The  $\frac{1}{2}(311)$  superstructure peak, which practically depends only on the oxygen rotation angle, was followed with temperature between 20 K and 360 K.

Precise pyroelectric discharge data have been obtained by means of a set-up specially designed to measure high

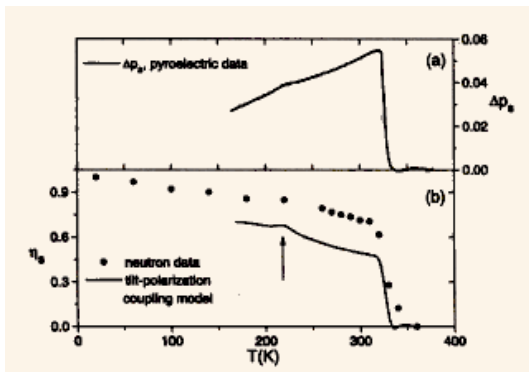


Fig. 2. (a)  $\Delta p_s$  vs.  $T$ , obtained subtracting  $p_s$  fit from  $p_s^{\text{total}}$  in Fig. 1. (b)  $\eta_s$  vs.  $T$ , from neutron data and predicted by Eq. (2). The arrow shows the place where the antiferroelectric phase could have taken place.

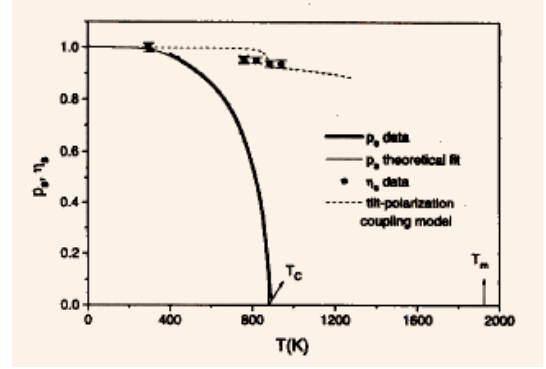


Fig. 3. Order parameters ( $p_s$  and  $\eta_s$ ) from pyroelectric current [8] and neutron data [9], respectively, are plotted versus temperature for  $\text{LiTaO}_3$ . The  $p_s$  fit was made by the generalised effective field approach. The dashed line shows the prediction of the perfect coupling model (Eq. (3)).

conductivity samples with a slow rate of temperature change. A detailed description of the system and its working scheme is given in a parallel work. Data shown in this work are taken during heating with a temperature rate of 20 K/h between 160 K and 600 K.

### III. RESULTS AND DISCUSSION

Very accurate polarization versus temperature measurements have been obtained in PZT. Normalised spontaneous polarization,  $p_s = P_s/P_{s0}$ , and tilt parameter,  $\eta_s = e_s/e_{s0}$ , have been plotted in Fig. 1, where  $P_{s0}$  and  $e_{s0}$  are, respectively, the spontaneous polarization and the tilt parameter at  $T=0$  K. The structural parameter  $e$ , is related to the tilt angle,  $\omega$ , by  $\tan \omega = 4\sqrt{3}e$ . The step in polarization at the  $F_{RL}$ - $F_{RH}$  phase transition,  $T_{LH}$ , can be clearly observed in the figure coinciding with the vanishing of the tilt.

The generalised effective field approach has been used

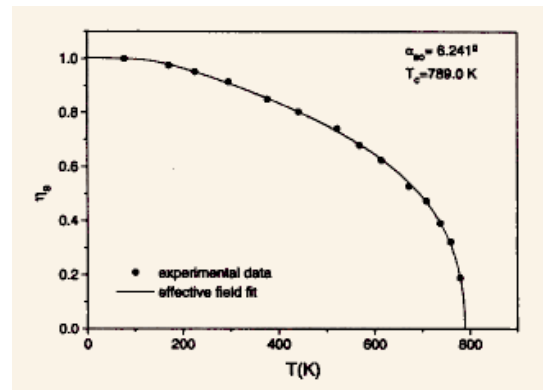


Fig. 4. Order parameter of  $\text{LaAlO}_3$  vs. temperature. The experimental data [7] are fitted with the generalised effective field approach.

to analyse the data. The conjugated effective electric field and staggered stress can be expressed as  $E_{\text{eff}} = E + \beta P + \gamma P^3 + \delta P^5 + \dots$  and  $|X_{\text{eff}}| = X + \beta_t \theta + \gamma_t \theta^3 + \delta_t \theta^5 + \dots$ , respectively, being  $E$  the external electric field,  $P$  the polarization,  $X$  the external stress and  $\theta$  the statistically resultant tilt. This theory leads to the following equation of state with  $E = 0$  ( $p = p_s$ )

$$\frac{T}{T_C} \frac{\tanh^{-1} p_s}{p_s} = 1 + g p_s^2 + h p_s^4 + \dots \quad (1)$$

where the parameters  $g, h, \dots$  describe the relative importance (to the dipolar term,  $\beta P$ ) of the higher order terms ( $\gamma P^3, \delta P^5 \dots$ ), and are proportional to the successive [3] even powers of  $P_{\text{so}}$  ( $P_{\text{so}}^2, P_{\text{so}}^4 \dots$ ). A fit of the experimental data of  $p_s$  vs.  $T$  by means of Eq. (1) is shown in Fig. 1.

The subtraction of the  $p_s$  fit to the experimental data is shown in Fig. 2(a). It gives us the behaviour with temperature of the normalised extra polarization,  $\Delta p_s$ , appearing due to the tilt.  $\Delta p_s$  reaches its maximum value at  $T_{\text{LH}}$  and should disappear at  $T = 0$  K.

A model to explain the tilt-polarization coupling was introduced in Ref. [3]. According to it, the tilt order parameter can be expressed in terms of  $p_s$  and  $\Delta p_s$  as

$$\eta_s = \frac{\Delta p_s}{1 - p_s(p_s + \Delta p_s)}. \quad (2)$$

$\eta_s$  is calculated from Eq. (2), being  $p_s$  and  $\Delta p_s$  those of Figs. 1 and 2(a), respectively.  $\eta_s$  is represented in Fig. 2(b) and compared to the experimental data. It can be seen the clear agreement between both structural data and model, in spite to the model simplicity. The arrow in the figure shows a peculiar behaviour at 220 K, which was attributed to the experimental error in previous work [3]. Nevertheless this small anomaly has been reproduced with the pyroelectric data through our coupling model. A new transition to an antiferroelectric (AF<sub>o</sub>) phase, at about the same temperature, has been recently proposed, but we have found here ferroelectric behaviour until 160 K. Our composition has similar Nb and Ti contents, and the phase diagram is still unknown in this region [10]. The tilt order parameter predicted by our model from the observed  $\Delta p_s$  is substantially smaller than the experimental one. This might be due to the fact that in a ceramic material the octahedra tilt may not be so efficiently coupled to the cation shifts as in a single crystal, as assumed for Eq. (2). On the other hand, Eq. (2) assumes perfect coupling in the sense that all the oxygen movement is reflected in the polarization behaviour. The validity of this assumption may depend in each particular case, on the cation charge and size, etc., as is manifested in LiTaO<sub>3</sub> (see below). The second case to be examined is LiTaO<sub>3</sub>, which does not reach the cubic perovskite structure (Pm3m) before melting. In this case the high temperature phase is not ferroelectric but possesses oxygen rotations. The low temperature phase has the same space group (R3c) as that PZT, with

both tilts and cation shifts. This is shown in Fig. 3, where  $p_s$  and  $\eta_s$  has been calculated from experimental data in Refs. [8] and [9], respectively.

The symmetry of the respective equations of state [3] for  $P - E$  and  $\theta - X$  allow us to follow, in the LiTaO<sub>3</sub> case, the same argument than before, interchanging  $\eta_s$  and  $p_s$ . So we have

$$\Delta \eta_s = \frac{1 - \eta_s^2}{1 + p_s \eta_s} p_s. \quad (3)$$

The  $\Delta \eta_s$  obtained from Eq. (3) with experimental data for  $p_s$  and  $\eta_s$  is plotted in Fig. 3 as a dashed line. In this case the coupling predicted by our model is not reflected in the available neutron data, within the experimental uncertainty. The high values of the tilt angle (about 22°) and cation shifts found in LiTaO<sub>3</sub> is a result of the weak interaction between Li<sup>+</sup> cations shifts and oxygen octahedra tilts, due to the small Li charge and size. This would leads to a weak, if any, observed tilt-polarization coupling. On the contrary, the large charge and size of the cations in PZT produces a strong coupling between the two order parameters, allowing a smaller maximum tilt angle of about 6°.

The case of LaAlO<sub>3</sub> is, however, an example of non-polar rhombohedral perovskite. Fig. 4 shows the experimental data of the order parameter [7] and the fit obtained by means of the effective field approach, in the whole temperature range, using the  $X - \theta$  equation of state [3].

In conclusion, we have contrasted the three observed possible sequences of phases with temperature of rhombohedral perovskites. Our data on PZT allow a more accurate test of the coupling between tilt and polarization. The possible weak coupling in LiTaO<sub>3</sub> has been discussed.

## ACKNOWLEDGMENTS

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